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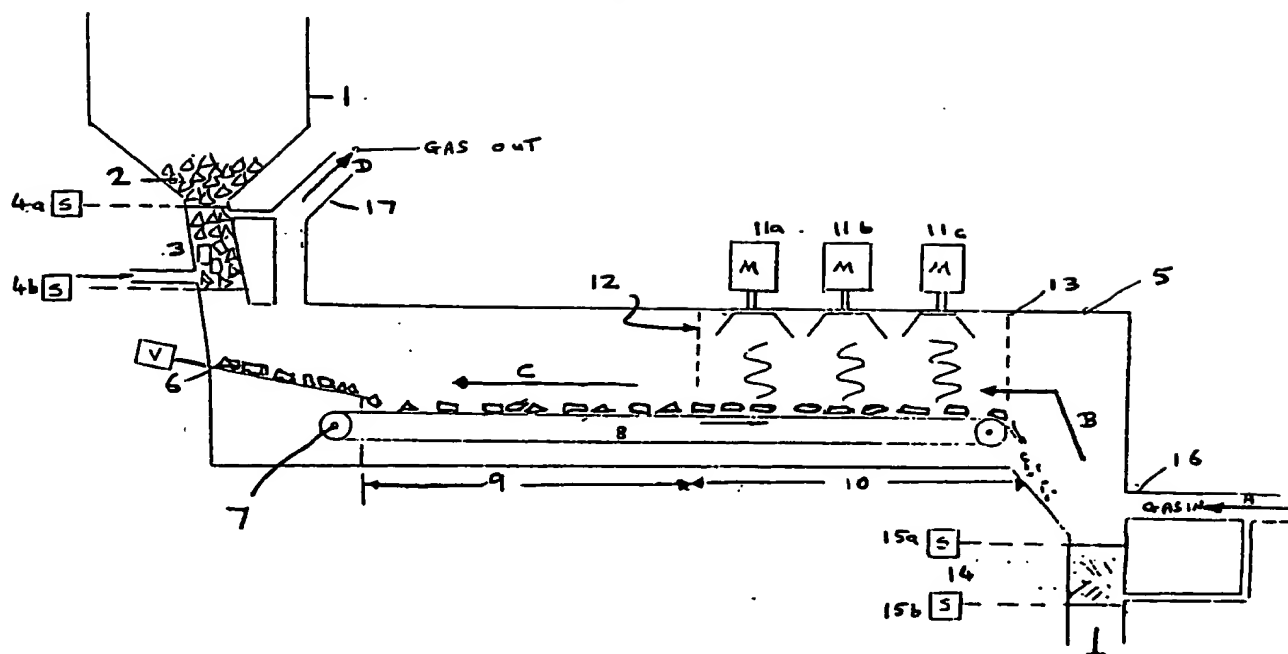
(71)(72) Applicant and Inventor: HOLLAND, Kenneth, Michael [GB/GB]; Ashwood, Wynwoods, Campbell Close, Rise Park, Ronford, Essex (GB).

(74) Agents: AUSTIN, Hedley, William et al.; Urquhart-Dykes & Lord, Alexandra House, Alexandra Road, Swansea SA1 5ED (GB).

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(54) Title: PYROLYSIS OF ORGANIC MATERIAL



(57) Abstract

The organic material (such as waste tyre compound) is pyrolysed by pre-heating the organic material (without pyrolysis) in a preheat zone (9) by a hot gas stream; feeding pre-heated material directly to a microwave discharge zone (10) by means of a conveyor (8); pyrolysing the pre-heated material in the microwave discharge zone to produce solid fission products containing elemental carbon and gaseous by-products; and recycling at least some of the latter to the hot gas stream which is supplied to the pre-heating zone.

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Pyrolysis of Organic Material

The present invention is concerned with the destructive distillation (or pyrolysis) of organic material, and particularly (but not exclusively), the pyrolysis of waste tyre material or other similar rubber compounds.

A process of pyrolysing organic waste by means of microwaves is disclosed in U.S. Patent 3843457; in this process organic industrial and household wastes are comminuted and the comminuted solid material is subjected to a microwave discharge in a gas stream at a pressure substantially less than atmospheric for a contact time of the order of one second. The gas stream and the comminuted solid material pass through the microwave zone in parallel, with a view to maximising interaction between the gas and the solid.

Microwave destruction of waste tyre material has also been disclosed in, for example, (examined) Japanese Patent Applications 76/47192-3, 77/26553, 82/3491 and (unexamined) Japanese patent applications 52/3672 and 51/123287. These documents describe laboratory scale processes, in which small quantities of the waste rubber are subjected to microwave discharge so as to completely break the rubber down and produce carbon black and hydrocarbons (gaseous or liquid). These documents give no details as to how the basic idea of microwave pyrolysis could be converted into a commercial process.

A more recent document, U.S. Patent 4647443, discloses a process of pyrolysing of waste tyre material which involves subjecting the tyre material to radiant heating so as to produce a pyrolysed char, and then subjecting the char to microwave discharge to remove volatile hydrocarbons from the char, so as to produce carbon black.

The disadvantage of this process is that radiant heating of tyre material involves relatively inefficient heat transfer. I have found that, contrary to the teaching of U.S. Patent 4647443, it is advantageous to pre-heat tyre material (and other organic materials), without pyrolysis thereof, prior to complete pyrolysis by means of microwaves. That is, microwave-induced pyrolysis has been found to be impaired if tyre material (or other organic material) has previously been partly pyrolysed (this is postulated to be because of the insulating effect of the elemental carbon produced on pyrolysis). It is believed that this may be why the U.S. patent teaches that the pyrolysis should be taken to substantial completion in the radiant heating stage.

I have now found that, in contradistinction to the teaching of U.S. Patent 4647443, it is advantageous to completely avoid pyrolysis in a pre-heating stage prior to microwave-induced pyrolysis.

The process according to the invention enables microwave pyrolysis of waste tyre material and other rubber compounds, as well as other organic materials, to be operated as a commercial destructive distillation process.

According to the present invention, therefore, there is provided a process of destructive distillation of organic material, which comprises:

- (a) pre-heating said organic material, substantially without pyrolysis of said organic material to elemental carbon, by means of a hot gas stream;

- (b) feeding said pre-heated material directly to a microwave discharge zone in an atmosphere of substantially oxygen-free gas which is above atmospheric pressure;
- (c) pyrolysing said pre-heated material in said zone by means of a microwave discharge of sufficient power, and for a sufficient time, to cause substantial fission of carbon-carbon bonds in the organic material, in addition to fission of more polar chemical bonds, so as to produce solid fission products containing elemental carbon, and gaseous by-products;
- (d) collecting said solid fission products downstream of said microwave discharge zone; and
- (e) recycling at least part of said gaseous by-products to said hot gas stream to effect said pre-heating.

The process according to the invention can be operated as a continuous process, as will be explained hereinafter.

It should, perhaps, be mentioned that a process involving the continuous microwave treatment of waste rubber material is known; see, for example, U.S. Patents 4104205 and 4129768, which are both concerned with devulcanisation of the rubber (that is, fission of carbon-sulphur bonds, but not of carbon-carbon bonds in the molecular structure). U.K. patent specifications 2028835 and 1513656 are similarly concerned with devulcanisation of rubber compounds by means of microwave irradiation. There is no hint or suggestion in any of these documents of the use of the conditions employed in the process according to the present invention for the purpose of substantial breakdown of carbon-carbon bonds.

In one embodiment of the invention, it is preferred that gaseous by-products should be recycled to function as the above-mentioned gas stream; it is also preferred that products in the nature of oils or other liquids

should be collected and, where appropriate, used as fuels to provide at least some of the energy input into the process.

The process according to the invention is directly contrary to the process described in U.S. Patent 3843457, in which it is suggested that in order to recover valuable products from solid waste which contains organic materials, one should subject the waste to microwave discharge while at reduced pressure and at less than 200°C; this appears to be because the waste material envisaged by the patentee comprises carbohydrates of which molecular fragments are reacted with an ionised gas, ionisation being caused by the microwave discharge.

In the process according to the invention, the material being subjected to destructive distillation is such that it contains a substantial proportion of carbon-carbon bonds (such as a hydrocarbon or carbohydrate material). Examples of such materials include natural or synthetic rubber compounds, and agricultural waste material such as citrus fruit peel, olive waste products, and nut shell (e.g. coconut shell), and animal waste (such as sewage, slurry or the like). The organic material is generally such that the solid fission products produced predominantly comprise elemental carbon.

In some embodiments (and particularly where the material being pyrolysed is a rubber compound), it is preferred that the organic material subjected to microwave discharge in the process according to the invention should contain carbon filler; a particularly preferred such material is waste tyre material. Waste tyre material pyrolysed according to the present invention may be in bulk or finely divided form (e.g. chopped form or pulverulent form). Such a material may contain, in addition to carbon filler, organic textile reinforcement and/or metal wire (e.g. steel wire) reinforcement.

When an organic textile material is employed, the latter is generally substantially carbonised in the discharge zone; when metal wire reinforcement is employed, the latter wire is substantially unaffected by the microwave discharge and is therefore collected together with the solid fission products.

In the process according to the present invention, the waste material is preferably pre-heated by means of the gas stream to a temperature of at least 250°C (such as 300 to 500°C) before being subject to the microwave discharge. It is particularly preferred that both the pre-heating stage and the microwave discharge stage should be carried out in a vessel (which is preferably thermally insulated and of suitable pressure rating) through which the organic material is passed on a conveyor in a continuous manner.

Typically, the same conveyor is used to forward the organic material through the pre-heating zone, to feed the pre-heated material to said microwave discharge zone, and to forward the pre-heated material through the microwave discharge zone. Such a conveyor may be, for example, an endless belt comprising stainless steel or the like.

Generally, it is preferred that the pre-heating zone and the microwave zone each have a purge lock both for supply of the organic material and for removal of solid fission products therefrom so as to substantially prevent inflow of oxygen-containing gas into the respective zone.

The gas stream used in the process according to the invention (which may be supplied in a countercurrent relative to the feed of organic material through the microwave discharge zone, or fed in the same direction) may additionally contain a separately supplied hydrocarbon or inert gas such as nitrogen, as well as at least some of the gaseous products of the destructive distillation. The gas stream may be continuously recirculated to the microwave discharge zone

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(preferably after scrubbing of the gas) and is in some embodiments (for example, where it is desirable to minimise microwave power input) at a temperature of at least 250°C (such as 300 to 500°C) when entering the microwave discharge zone.

The microwave discharge used in the process according to the invention may be in the low gigahertz frequency range (e.g. about 2.4 gigahertz). The duration of the microwave irradiation phase is typically about 15 to 60 minutes; this will depend largely on the nature of the material to be pyrolysed.

Reference will now be made to the accompanying drawings, in which:

Figure 1 is a schematic illustration of an exemplary embodiment of the pyrolysis process according to the invention; and

Figure 2 is a more detailed flow diagram of a further embodiment of the process according to the invention.

Referring to Figure 1, there is shown a feed hopper 1 which is charged with chopped waste rubber material 2. Towards the base of hopper 1 is a purge lock 3 comprising an upper gate 4a and a lower gate 4b, which can be operated so as to prevent, or at least minimise, inflow of air when the rubber material is charged to an insulated vessel 5.

As rubber material is charged from the hopper 1, it falls into a vibrating feed and spreader 6, which itself causes the chopped material to be forwarded to the drive end 7 of belt-type conveyor 8 where the material is preferably spread as a bed of a predetermined depth. As illustrated, the drive end of the conveyor 8 is located in a pre-heating zone 9 of the vessel 5. In the pre-heating zone, the chopped material is typically raised to a temperature in the range 300 to 500°C.

Downstream of the pre-heating zone 9 is a microwave discharge zone 10 having a plurality of microwave

sources 11a, 11b, 11c. These sources may be all of substantially similar power output, or, alternatively, of graduated power output (for example, of gradually increasing power output with distance from the pre-heating zone 9). The microwave zone 10 is separated from the pre-heating zone 9 by a microwave shield 12; there is a further such shield 13 downstream of the conveyor 8. Further downstream still is a second purge lock 14 comprising an upper gate 15a and a lower gate 15b; solids from the downstream end of the conveyor 8 pass directly to the second purge lock, from where solids produced may be collected.

The vessel 5 is further provided with a gas inlet 16 for hot circulating gas, which passes in the direction of arrows A,B,C,D, and a gas outlet 17 for the gas. The gas supply is controlled such that the gas pressure in the vessel is superatmospheric. In the illustrated embodiment of Figure 1, the inlet 16 and the outlet 17 are so arranged that the gas flows in countercurrent through the microwave discharge zone 10 and then through the pre-heating zone 9.

Referring to Figure 2, there is shown a process in which waste tyre material 18 is fed to a shredder 20 and the shredded material passed by a feed conveyor 22 to a hopper 24 (oversized material being recycled via line 25 to shredder 20) and then via purge chamber 26 having a series of three purge lock gates 27 to a reactor 28 having a heat resistant conveyor 30 passing therethrough. The conveyor 30 extends from a first upstream end 32 of the reactor 28, which functions as a pre-heating zone, to a second, downstream end 34 provided with microwave sources 36, in which the tyre material is pyrolysed to fission products containing elemental carbon.

The fission products pass from the downstream end 34 of the reactor 28, through a further purge chamber 38 having a series of three purge lock gates 39, via crush rolls 40 to a magnetic separation zone 40, from which steel scrap is collected

at outlet 42; the remaining pyrolysed material is passed through a cooling zone 44 to be collected downstream at 46.

Nitrogen is fed via lines 48 and 50 to each of the purge chambers 26 and 38 so as to ensure that there is an oxygen-free atmosphere, at superatmospheric pressure, in the reactor 28.

The reactor 28 is further provided with a gas circulation circuit, in which gas is introduced via inlet 52 upstream of the downstream end 34 of the reactor, and allowed to exit via outlet 54 downstream of the microwave zone. From outlet 54, the gas passes to a quench cooler 56 and thence to a quench column 58.

Bottoms from the latter are recycled via recirculating oil pump 60, filter 62, and oil cooler 64 to the top 66 of quench cooler 56, part of the stream from the filter 62 being passed to stripper 68 supplied with steam 70. Bottoms from the stripper 68 are passed via oil pump 72 and heat exchanger 73 to storage tank 74; volatiles from the stripper 68 are recycled to quench column 58. Volatiles from column 58 are passed via heat exchanger 76 to decanter 78, where separation is effected into effluent 80 (for disposal), liquids 82 (passed via pump 84 to storage tank 86 for mixing with oil from tank 74) and gases 88. A portion of the gas is recycled via blower 90 and gas heater 92 to inlet 52; the remainder of the gas is drawn off at 94 to be used for power generation or the like. (In Figure 2, "CW" represents the supply of cooling water to the respective heat exchanger.)

CLAIMS:

1. A process of destructive distillation of organic material, which comprises:
 - (a) pre-heating said organic material, substantially without pyrolysis of said organic material to elemental carbon, by means of a hot gas stream;
 - (b) feeding said pre-heated material directly to a microwave discharge zone in an atmosphere of substantially oxygen-free gas which is above atmospheric pressure;
 - (c) pyrolysing said pre-heated material in said zone by means of a microwave discharge of sufficient power, and for a sufficient time, to cause substantial fission of carbon-carbon bonds in the organic material, in addition to fission of more polar chemical bonds, so as to produce solid fission products containing elemental carbon, and gaseous by-products;
 - (d) collecting said solid fission products downstream of said microwave discharge zone; and
 - (e) recycling at least part of said gaseous by-products to said hot gas stream to effect said pre-heating.
2. A process according to claim 1, in which the same feed means is used to forward said organic material through the pre-heating zone, to feed said pre-heated material to said microwave discharge zone, and to forward said material through said microwave discharge zone.
3. A process according to claim 1 or 2, in which the pre-heating zone and the microwave zone each have a purge lock for respective supply and removal of solid material therefrom without inflow of oxygen-containing gas into the respective zone.

4. A process according to any of claims 1 to 3, wherein said gas stream comprises substantially the entirety of gaseous by-products, passed in countercurrent to the feed of said organic material.
5. A process according to any of claims 1 to 3, wherein said gas stream comprises at least part of said gaseous by-products which have been recycled such that the gas stream and the organic material pass through the microwave discharge zone in the same direction.
6. A process according to claim 4 or 5, wherein said gas stream further comprises separately supplied hydrocarbon or nitrogen.
7. A process according to any of claims 1 to 6, wherein liquid by-products from the microwave discharge zone are burnt and the resultant thermal energy is used to provide at least some of the energy input into the process.
8. A process according to any of claims 1 to 7, in which said organic material predominantly comprises hydrocarbon and/or carbohydrate materials.
9. A process according to any of claims 1 to 8, wherein said organic material comprises a rubber compound, preferably containing carbon filler.
10. A process according to claim 8, wherein said organic material comprises waste matter derived from animals or plants.

INTERNATIONAL SEARCH REPORT

International Application No **PCT/GB 88/00979**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁴: C 10 B 53/00

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

| Classification System | Classification Symbols |
|-----------------------|------------------------|
| IPC ⁴ | C 10 B |

Documentation Searched other than Minimum Documentation
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

| Category ⁹ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
|-----------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|
| Y | US, A, 4647443 (APFFEL) 3 March 1987, see claims 1,15-24; figure 1A (cited in the application) -- | 1,3-10 |
| Y | US, A, 3843457 (GRANNEN et al.) 22 October 1974, see claims 1,2,5,7-9; column 2, lines 62-70 (cited in the application) -- | 1,3-10 |
| A | US, A, 3449213 (KNAPP et al.) 10 June 1969, see claim 1; figure 3 -- | 1 |
| A | Database WPIL, Derwent, see abstract no. 73-66277U & JP, B, 76047192 (AGENCY OF IND. SCIENCES AN) 12th December 1976 (cited in the application) ----- | 1 |

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IV. CERTIFICATION

Date of the Actual Completion of the International Search

15th February 1989

Date of Mailing of this International Search Report

14. 03. 89

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Signature of Authorized Officer

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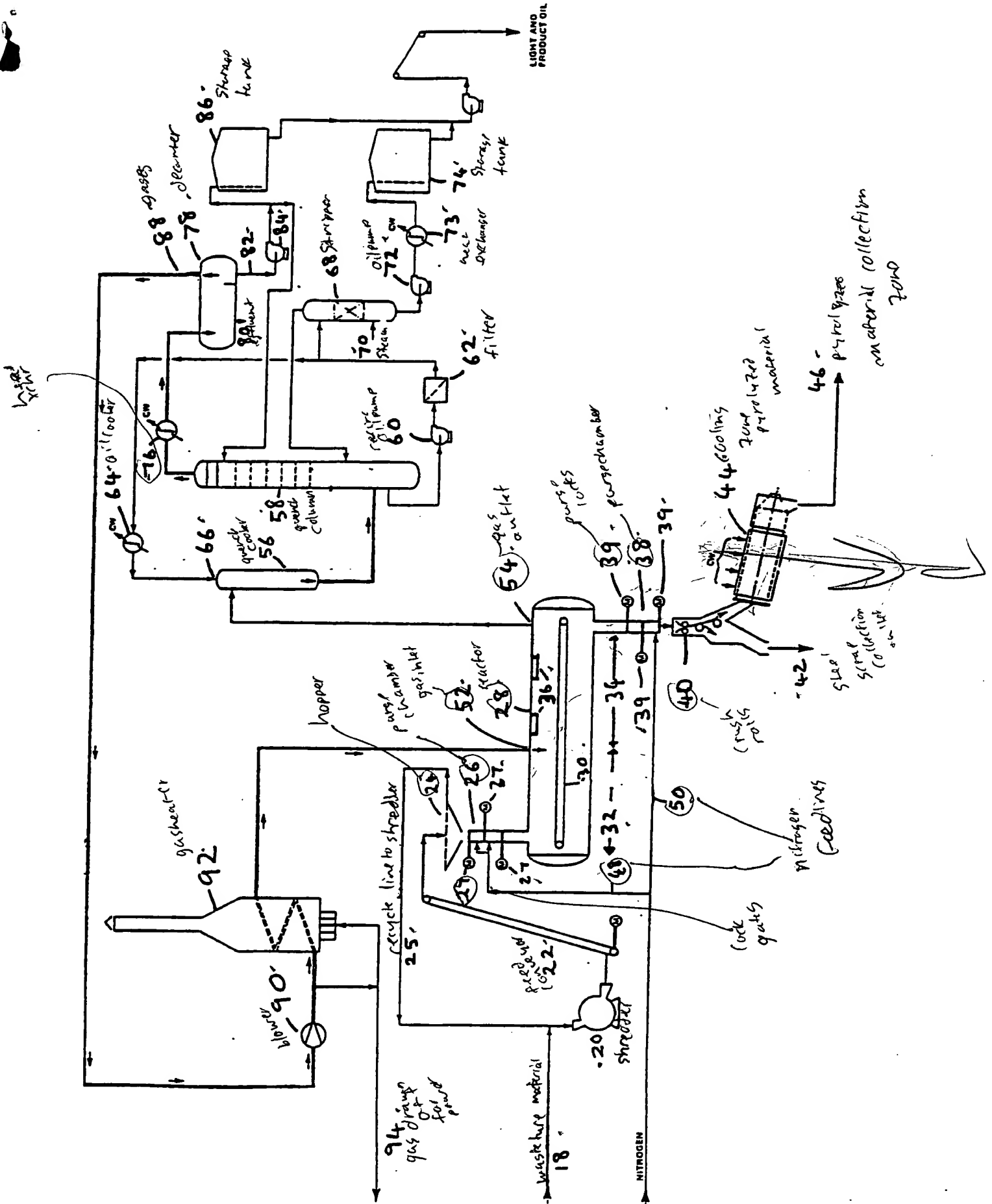
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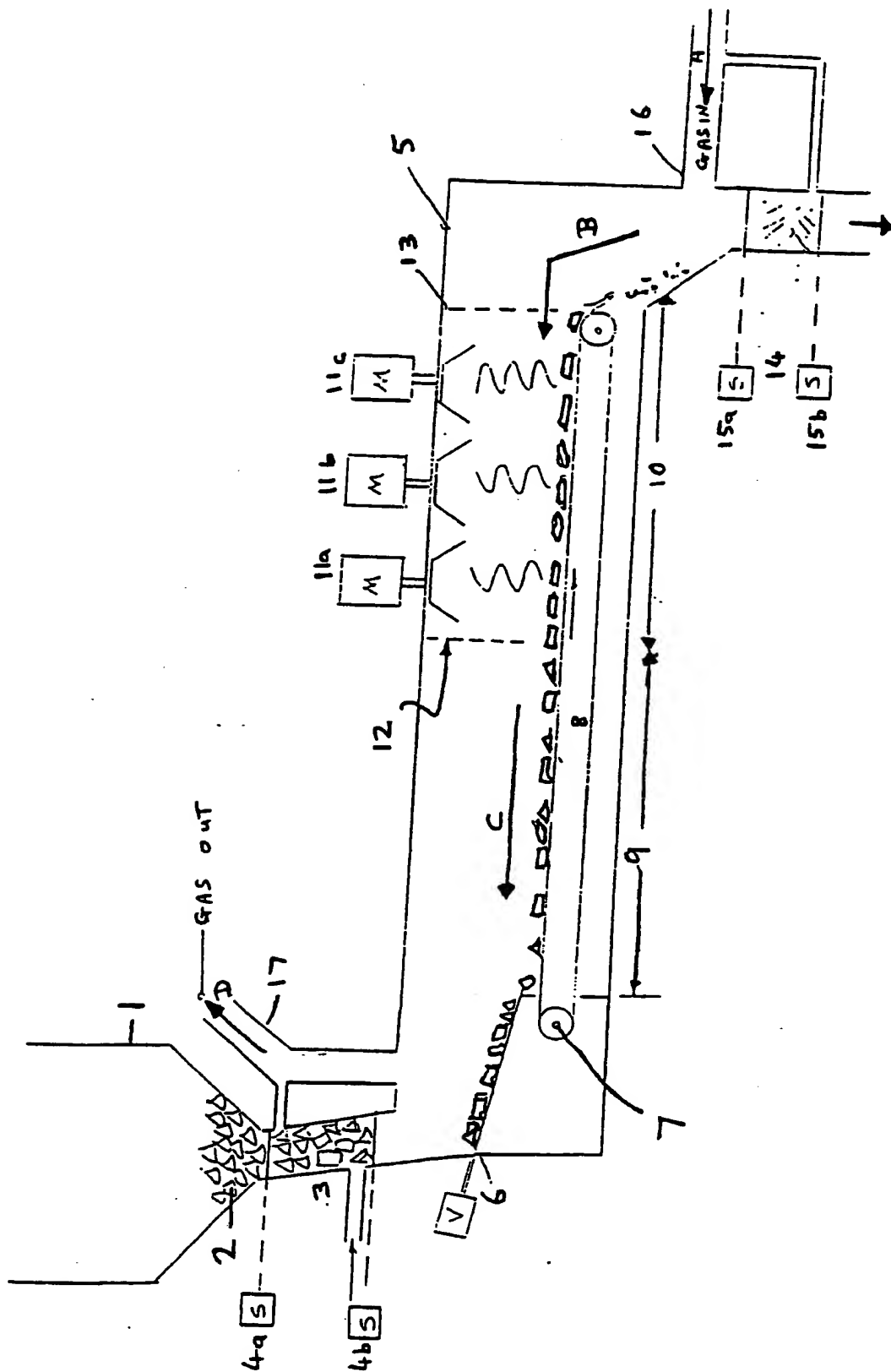
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| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|-------------------------------------------|---------------------|----------------------------|---------------------|
| US-A- 4647443 | 03-03-87 | None | |
| US-A- 3843457 | 22-10-74 | None | |
| US-A- 3449213 | 10-06-69 | US-A- 3523405 | 11-08-70 |
| | | US-A- 3560347 | 02-02-71 |





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